C-O-N-F-I-D-E-N-T-I-A-L	SEE BOTTOM OF PAGE FOR SPECIAL CONTROLS, IF ANY

INFORMATION REPORT

PREPARED AND DISSEMINATED BY

CENTRAL INTELLIGENCE AGENCY

25X1

COUNTRY

Hungary

SUBJECT

The Iron Industry Research Institute in Budapest/
Organization including Departments for Cast Iron,
Steel and Steel Alloys, Pig Iron and Ores Processing,
Powder Metallurgy, Welding Research, Material Testing,

DATE DISTRIBUTED 28 Jan 58

NO. OF PAGES 2

NO. OF ENCLS.

SUPPLEMENT TO REPORT #

25X1

25X1

and Cryo.. **THIS IS UNEVALUATED** INFORMATION

25X1

25X1

1. The designation of the institute was Vasipari Kutato Intezet (Iron Industry Research Institute). It was a subordinate agency of the Koho Es Gepipari Miniszterium (The Ministry of Foundries and Machine Industry) was still subordinated to the same agency The institute was located in a modern building, on the northwest corner of Fehervari Ut and Andor Utca, Budapest XI, with the main entrance to the institute being located at 130 Fehervari Ut.

2. The institute was responsible for various types of advanced research conducted under the guidance of the Ministry of Foundries and Machine Industry for the purpose of satisfying urgent industrial requirements. It was divided in the following major sections or departments: (a) Cast Iron Department; (b) Steel and Steel Alloys Department; (c) Pig Iron and Ores Processing Department; (d) Powder Metallurgy; (e) Welding Research; (f) Material Testing (Microscopic and Mechanical Testing); (g) Chemico-analytical Department; and (h) Administrative Section. Approximately 12 persons with professional qualifications, among them from five to six fully qualified engineers, composed the nucleus of each department.

25X1

3. The facility at 130 Fehervari Ut occupied by the institute, was a very modern structure completed in 1951. It was a two-story building with additional office space located in the basement. The building was equipped with all modern facilities, such as gas, electricity, running hot and cold water and central heating system.

4. Between 200 and 250 personnel were employed by the institute including the scientific staff. Dr Jozsef Vero, an allegedly internationally known metallurgist and Professor at the Technological Institute of Miskolc (4806N 2047E), was in charge of the institute, commuting between two institutions every other day.

USAF review completed.

C-O-N-F-I-D-E-N-T-I-A-L

25X1

C-O-N-F-I-D-E-N-T-I-A-L

-2-

5. Approximately half of the building occupied by the institute was evacuated shortly before December 1956 for the purpose of accommodating another research organization, which I would possibly identify as Aluminum Research Institute.

25X1

the new organization was equipped with instruments required for spectral analysis and microphotography as applicable to mineral technology.

6. Each candidate for a Ph D degree or membership in the Hungarian Academy of Science had a choice of four languages (Hungarian, German, Russian, and English) in writing his thesis

25X1

/On File   are:

25X1

    (a) Photostatic copy of scientific paper "Surface Pattern of Spherical Shell Graphite", eight pages. Unclassified.

    (b) Photostatic copy of scientific paper "On the Crystallization of Graphite in Cast Irons", 31 pages. Unclassified./

-END-

C - O-N-F-I-D-E-N-T-I-A-L

25X1

Page Denied

TECHNICA

ENTIARUM HUNGARICAE

FASCICULI 3 — 4

I. KARSAY

Pattern of Spherical Shell Graphite

BUDAPEST

1956

SURFACE PATTERN OF SPHERICAL SHELL GRAPHITE

I. KARSAY

CANDIDATE OF ENG. SC.

INDUSTRIAL IRON AND STEEL RESEARCH INSTITUTE, BUDAPEST

In a former paper [Öntőde (Foundry), No. 8—9, 1955, pp. 169. and 205., in Hungarian] the author gave account of his observation that under

certain circumstances graphite crystallizes in cast iron in hollow, spherical shell structure. A characteristic pattern is visible on the surface of this spherical shell graphite.

Latest investigations have found that the pattern consists of concentric circles (see Fig.).

By reason of the same investigations it is probable, though not proven, that the pattern is not correlated with the crystallization of graphite, but with

Surface pattern of spherical shell graphite 550x.

15*

that of austenite. That is to say, after removal of the graphite shell the lines appear on the iron surface too ; the graphite shell is only modeled in full thickness according to the wrinkles of the iron surface.

It has to be pointed out that the afore-mentioned pattern has so far been recognizable only on spherical shells developed in magnesium-treated cast irons ; the surface of spherical shells of other kinds of iron is smooth.

СТРУКТУРА ПОВЕРХНОСТИ ПОЛОГО СФЕРОИДАЛЬНОГО ГРАФИТА

Канд. техн. наук И. КАРШАИ

В опубликованной автором ранее статье [Öntöde(Литейное производство) 1955, 8 и 9, стр. 169, соотв. 205, на венг. яз.] указано, что при определенных условиях в чугуне кристаллизируется полый шаровидный графит. На поверхности этого шаровидного графита наблюдается характерная структура.

Последними исследованиями установлено, что структура представляет собой концентрические круги (см. рис.).

На основе этих же исследований вероятно, — хотя еще не доказано, что наблюдавшаяся структура связана не с кристаллизацией графита, а с кристаллизацией аустенита. Структурные линии после удаления графитовой оболочки наблюдаются также на поверхности металла, графитовая же оболочка во всей своей толще лишь повторяет структурную форму на поверхности аустенита.

В дополнение к этому следует еще указать, что упомянутую выше структуру до сего времени удалось показать только на шаровых оболочках, образовавшихся в чугуне, обработанном магнием, поверхность же оболочек шаровидного графита других сортов чугуна гладкая.

DESSIN DE LA SURFACE DU GRAPHITE EN COQUE SPHÉRIQUE

J. KARSAY

Candidat ès sciences techniques

Dans une étude antérieure [Öntöde (»Fonderie«), No. 8, 9, 1955, pp. 169 et 205 en hongrois.] l'auteur a rendu compte de l'observation que dans certaines conditions le graphite se cristallise dans la fonte en coques sphériques vides à l'intérieur.

Les recherches les plus récentes ont démontré que le dessin de cette structure consiste en des cercles concentriques (v. fig).

À la base des mêmes études il est probable, bien qu'il ne soit pas prouvé, que ce dessin est en corrélation non pas avec la cristallisation du graphite, mais avec celle de l'austénite. En effet les lignes existent sur la surface du fer aussi, après l'élimination du graphite. La coque de graphite se modèle seulement sur les rides de la surface de fer en toute son épaisseur.

Il faut noter encore que ce dessin n'a été constaté jusqu'ici que sur les coques sphériques développées dans de la fonte traitée par l'addition de magnésium, tandis que la surface des coques sphériques de graphite des autres espèces de fonte est lisse.

DAS OBERFLÄCHENMUSTER DES KUGELSCHALENFÖRMIGEN GRAPHITS

I. KARSAY

Kandidat der technischen Wissenschaften

Der Verfasser hat in einer früheren Arbeit (»Öntöde« [Giesserei] 1955, Nr. 8, S. 169 und Nr. 9, S. 205, nur ungarisch) darüber berichtet, dass im Gusseisen unter gewissen Umständen ein innen hohler, kugelschalenförmiger Graphit kristallisiert. Auf der Oberfläche dieses Kugelgraphits ist ein charakteristisches Muster zu beobachten.

Die neuesten Untersuchungen haben ergeben, dass dieses Muster aus *konzentrischen Ringen* besteht (vgl. Abb.).

Auf Grund derselben Untersuchungen erscheint es als wahrscheinlich — wenngleich noch nicht als erwiesen —, dass das Muster nicht mit der Kristallisation des Graphits, sondern mit der des Austenits zusammenhängt. Die Linien sind nämlich auch nach der Entfernung der Graphitschale auf der Eisenoberfläche zu sehen, die Graphitschale folgt also in ihrer ganzen Dicke der Faltung der Eisenoberfläche.

Es ist zu bemerken, dass es bisher nur an Kugelschalen, die sich in dem mit Magnesium behandelten Eisen gebildet haben, gelungen ist, das erwähnte Oberflächenmuster nachzuweisen, während die Oberfläche der Graphitkugelschalen anderer Eisensorten glatt ist.

Acta Technica
Budapest M. Pf...

Toute correspondance doit être envoyée à ...

Le prix de l'abonnement est de 120 Ancbs ...

On peut s'abonner à l'Observation près la Compagnie d'Editions de Livres et Journaux «Kultura» (Budapest, VI., Szabó 21. de Compte ... 181) ou à l'étranger chez tous les représentants ou dépositaires.

The *Acta Technica* ... ... in Russian, French, English and German ...

... ... making up one volume.

Acta Technica
Budapest 62, ...

... correspondence with the editors and publications should be sent to the same address. ... ... of subscription to the *Acta Technica* is 120 forints a volume. Orders may ... ... Foreign Trade Company for Books and Newspapers (Budapest, ... Account No. 43-790-057-181) or with representatives abroad.

... ... persönlichen Abhandlungen aus dem Bereiche der technischen ... ..., französischen, englischen und deutscher Sprache.

... erscheinen in Heften wechselnden Umfanges, Mehrere Hefte bilden ... ...

... bestimmten Manuskripte sind mit Maschine geschrieben, an ... ...

Acta Technica
Budapest 62, Pf... ...

An ... gleiche Anschrift ist auch jede für die ... ... und den Verlag bestimmte Korrespondenz ...

... ... pro Band 120 Forint. ... ... zum Buch- und Zeitungs-Aus-... «Kultura» (Budapest, VI., ... Konto-Nr.43-790-057-181) oder bei ihren Auslandsvertretungen und Kommissionären.

ACTA TECHNICA

A MAGYAR TUDOMÁNYOS AKADÉMIA
MŰSZAKI TUDOMÁNYOK OSZTÁLYÁNAK
KÖZLEMÉNYEI

SZERKESZTŐSÉG ÉS KIADÓHIVATAL: BUDAPEST, V., ALKOTMÁNY UTCA 21

Az Acta Technica orosz, francia, angol és német nyelven közöl értekezéseket a műszaki tudományok köréből.

Az Acta Technica változó terjedelmű füzetekben jelenik meg. Több füzet alkot egy kötetet, 3—4 kötet alkot egy évet.

A közlésre szánt kéziratok, géppel írva, a következő címre küldendők:

Acta Technica, Budapest 62, Postafiók 440.

Ugyanerre a címre küldendő minden szerkesztőségi és kiadóhivatali levelezés.

Az Acta Technica előfizetési ára kötetenként belföldre 80, külföldre 110 Ft. Megrendelhető a belföld számára az Akadémiai Kiadónál (Budapest, V., Alkotmány utca 21. Bankszámla 05-915-111-46), a külföld számára pedig a „Kultúra" Könyv- és Hírlap Külkereskedelmi Vállalatnál (Budapest, VI., Sztálin út 21. Bankszámla: 43-790-057-181), vagy annak külföldi képviseleteinél és bizományosainál.

Acta Technica публикуют трактаты из области технических наук на русском, французском, английском и немецком языках.

Acta Technica выходят отдельными выпусками разного объема. Несколько выпусков составляют один том.

Предназначенные для публикации рукописи (в напечатанном на машинке виде) следует направлять по адресу:

Acta Technica, Budapest 62, Postafiók 440.

По этому же адресу направлять всякую корреспонденцию для редакции и администрации.

Подписная цена «Acta Technica» — 110 форинтов за том. Заказы принимает предприятие по внешней торговле книг и газет «Kultura» (Budapest, VI., Sztálin út 21. Текущий счет № 43-790-057-181), или его заграничные представительства и уполномоченные.

ON THE CRYSTALLIZATION OF GRAPHITE
IN CAST IRONS*

I. KARSAY

CAND. TECHN. SC.

HUNGARIAN RESEARCH INSTITUTE OF THE IRON AND STEEL INDUSTRY

1. Introduction

The problem of the crystallization of graphite in grey cast irons is a very much discussed one, and in the past 50 years scientific papers, related with this theme, have appeared in an incessantly increasing number. There is perhaps no other question in the field of metallography, where so many contradictory views are still conflicting each other. It is, however, hardly conceivable to have a troublefree commercial production or to be able to control securely the various factors, which affect the same, without the clearing up of the theoretical aspects of the crystallization of graphite. Just this shows the practical significance of the outlined problem.

Great efforts have already been produced to give a comprehensive explanation, made during the experiments or in the practice and related with this question. The various explanations are, however, generally in contradiction, not only to each other, but to some observed phenomena too. There are also some observations, for instance some of the author's as well, for which there lacks any explanation.

It is therefore principially just and scientifically permissible to evolve a new hypothesis. This is set down in the last section of this paper and is based partly on observations, made during the experiments conducted by the author, but mostly on theoretical and practical experiences gathered in the past. The said hypothesis explains principally all the observations made by any investigator. It is nevertheless not absolutely — especially in all details — accurate.

2. The review of the literature

As already mentioned in the Introduction, several explanations and by numerous authors were developed for the crystallization of graphite in cast irons. Even a short summary of their work would make this paper out of proportions, and the author wishes to undertake only a critical review of 3 main problems, which are especially important in view of the following interpretations. Even this review could be made only a limited one.

* Abridged version of the author's thesis, submitted in partial fulfilment of the requirements for the degree of Candidate of Technical Sciences at the Hungarian Academy of Sciences.

7*

L. KARSAY

2.1 The problem of the shape of the graphite flakes

There are very few notes, dealing with this question. The greatest part of the authors take it for granted that the solidification of the molten cast iron leads to flake-graphite.

Essentially there exists only a single explanation for the formation of graphite flakes. According to this, the crystallization has preferred directions in wich to propagate at very high rates, and this is made possible by the structure of the crystal lattice of the graphite — this difference in the crystallization rate leads then to the flaky shape.

This explanation is however far from being satisfactory. It is nevertheless a fact, that the formation of a new unit cell in the direction of the axis of the lattice makes necessary the arrangement of 6 carbon-atoms, whereas for the formation of a new unit cell in the direction of the basal plane we need to have only 4, 3 or 2 and in some cases only a single carbon-atom. The probability for a growth in the direction of the basal plane is therefore 6—1 1/2 times as great as in the direction perpendicular to that, and in reality is still much greater, because 2 or 3 atoms may be arranged much easier than 6.

We come to the same conclusion, if we are examining the question of the binding forces. The consecutive basal planes are bound only by very weak forces to each other. The formation of an entirely new basal plane makes therefore necessary the corresponding positioning and grouping of much more atoms, than the further growth of an already existing basal plane. In the last case we have a probability of about 50% for a "superficial equilibrium" of the new atom. (On two of the neighbouring corners there are already located carbon atoms.) Even if it is not so, each atom arriving in the basal plane is bound by covalent forces, which are in any case much greater, than the bonding forces perpendicular to that plane, the so-called VAN DER WAALS forces[1].

It is therefore quite obvious, that the dimensions of the basal planes of the graphite particles are always greater than those perpendicular to that plane. This is, however, far from giving a satisfactory explanation for the formation of flake-graphite.

Should the ratio of the various dimensions really be governed by the laws of statistics, then there lacks an explanation for the great fluctuation of the same ratio. The ratio of the length to the thickness of the graphite flakes varies usually between 3 : 1 and 200 : 1. It is very curious that the greatest flakes are generally the thinnest ones. There also lacks any explanation as to why there are encountered so few graphite flakes with polygonal circumference : if the formation of the same would really be governed by the laws of crystallization, one should expect to find a hexagonal shape of the graphite.

The above explanation is especially insufficient in view of the fact, that the graphite flake is not a monocrystal, but a grouping of crystallites.

PIWOWARSKY and WITTMOSER [2] made X-ray examinations and have shown the linear dimensions of the crystallites of the graphite of cast irons being of the order of 10^{-7} cm. Supposing the shape of the crystallites to be cubical, a graphite plate with a diameter of 100 μ and a thickness of 5 μ would be made up by a number N of crystallites

$$N \frac{\frac{\pi}{4}(10^{-2})^2 \cdot 5 \cdot 10^{-4}}{(10^{-7})^3} \quad 3.9 \cdot 10^{13}.$$

In reality, it is very probable that the crystallites are also lamellar and N is therefore more probably somewhat less.

Accepting as a fact — which is hardly disputable — that the hypereutectic graphite crystallizes directly from the melt, it is quite unintelligible, why the crystal nuclei are not randomly distributed in the melt, but are highly concentrated in relatively small — and periodically repeated — volumes and are later grouped into homogeneous graphite flakes. It is still stranger, why these plates, growing out from a great mass of crystal nuclei, are perfectly parallel to each other. It is notably a fact, that the crystallites of a graphite plate are in an arranged state because their (0001) indexed planes are always parallel to the basal plane of the graphite plate. The proof of the same can be attained very easily by magnetic measurements.

The enumerated facts cannot be omitted when considering the problem of the shape of the graphite flake.

2.2 The problem of the spheroidal shape

In contrary to the aforementioned problem, the literature related with the "spheroidizing" problem is very abundant. The most common explanation relates the spheroidal shape with some "unkind" nuclei. A hexagonal (kind or unkind) nucleus grows into a flake, whereas a cubic nucleus leads to spheroidal graphite [3]. Although there remained but a few adherents to this view, it is worth while to deal shortly with this question.

/

Modern metallography highly appreciates the crystal nuclei or — what is almost the same — some "approximately arranged atomic groupings" within the melt. The dimensions of the primary grains depend mostly on the amount of the said nuclei. It is also conceivable that the lack of these nuclei is suppressing the crystallization of some phases. (Nuclear hypothesis of the Fe-C diagram-twins.) According to our knowledge, however, we cannot give a satisfactory explanation as to how some nuclei, which represent the outset of the crystallization, could be made responsible for the alteration of the shape of a grain in such a way as it happens in the case of spheroidal graphite. The nuclei may indicate as to where the first crystallites are likely to be formed in the melt, and the increasing amount of nuclei may lead to the decrease of the dimensions of the grain, but they can hardly be made responsible for the alteration of the flaky form into a spheroidal one. It is therefore quite out of place to speak of some nuclei which "favour the formation of spheroidal graphite".

A very interesting opinion is that of GILLEMOT [4], according to which ferrosilicon, used for secondary inoculation, results in some parts of the melt being spheroidal, saturated with silicon and of hypereutectic concentration, in the centre of which places the graphite may segregate in the form of small spheres. Making some calculations on the alteration of the concentration-gradient as a function of time, we find a surprising conformity between the dimensions of these small spheres of hypereutectic concentration and those of the graphite spheres. There is no doubt, however, that spheroidal graphite can be made to crystalline out from a pseudo-homogeneous material [5], without any inoculation with FeSi and this fact could hardly be explained with the help of the said hypothesis.

Graphite formed indirectly has always the shape of a sphere or of a spheroid, according to the opinion of GIRSHOVITCH [6]. The form of the graphite is controlled, according to him, in this case not by the crystallization, but by the conditions for the diffusion of carbon and a diffusion around a nucleus is always spherically symmetrical. The weak point of this reasoning lies in the fact, that tempering at high temperatures may lead to flake graphite too [2, 7]. If we accept, as Girshovitch claims, that the alloy is at this high temperature in a quasi-liquid state, then it must be much more liquid in the temperature range of eutectic solidification or at a temperature just below the eutectic temperature, even after a treatment with Mg.

There is another opinion, according to which the interdendritic residual melt gets highly saturated in carbon and this should be made responsible for the formation of spheroidal graphite [9]. This view neglects, however, to answer just the most important question as to why should this be responsible for the same.

A very imposing and now favoured explanation is based on the great surface tension of the melt which should force the graphite to take the form of a sphere. The formation of spheroidal graphite was compared by THALL and CHALMERS [10] with the modification of the Al-Si alloys by sodium. It is out of question that the treatment of the iron melt with Mg causes an increase of about 50% in the surface tension of the same [11]. But it is also out of question, that spheroidal and flake graphite may be produced within the same material and at the same time. Variation of the cooling rate may result in a part of the sample having graphite in the form of spheroids, while the other part of the same sample may have graphite in the form of flakes (see Fig. 2). The surface tension of a melt is everywhere the same, because it is quite independent of the cooling rate. It may be concluded therefore that the surface tension may exercise only a secondary effect on the shape of the graphite.

Mg forms an adsorbing envelope around the graphite, according to BUTTNER, TAYLOR and WULFF [12], and this prevents the obeyance to the laws of crystallization. On the other hand, CORRAL [13] explains the formation of the sphere with the cleaning action of Mg on the boundary of the different phases. Neither idea is based on experimental observations, but on close examination we may find that both attribute the spheroidal shape of the graphite to the increase of surface energy. This explanation is, however, as already discussed, not a sufficient one.

More and more investigators are imagining the crystallization of the graphite as a process, which takes place from a supersaturated solid solution. The investigations of WITTMOSER [14] gave a real proof of the fact, that the spheroidal graphite is formed always in the primary dendrites of austenite. This fact gives, however, no explanation as to why it takes the form of spheres.

The most up-to-date conception of crystallization of the graphite out of a supersaturated solid solution is the hypothesis of BUNIN. His fundamental idea [15] is that the formation of graphite first of all requires some vacant place. Crystallization of the graphite can take place only in those places, which are made free for it by the iron atoms. Thus — according to Bunin the controlling factor of the crystallization of graphite is the self-diffusion of the iron atoms.

This fundamental idea was further developed by two new papers. The first of them is that of LICHTMAN [16]. He proves by his experiments that the decomposition of cementite is a very rapid process, if porous products of powder metallurgy are being annealed. This "ultra-

rapid" decomposition of the cementite was explained by Lichtman on the basis of the hypothesis of Bunin. Lichtman supposes that the graphite finds already some ready made cavities in this porous material and thus there is no need for the self-diffusion of the iron-atoms. That is the reason why this process is so rapid.

Last of all a new paper of BUNIN [17] gives a very interesting proof for the pronounced effect the cavities exert on the crystallization of graphite. He succeeded to produce white iron consisting entirely of ledeburite and always being porous, though not to a great extent. This iron he annealed for a long time at a high temperature in order to secure the decomposition of the cementite. He observed already after the first 24 hours, that the nascent carbon atoms were penetrating into the cavities and formed there graphite. These cavities became filled up entirely by graphite. The continuation of these experiments is especially interesting. He continued the annealing after the filling up of the cavities, at the same temperature (1100 C) and for 72 more hours and found no further graphitisation. This illustrates that after the filling up of the cavities there is no further decomposition of cementite ; the same is very stable.

Not even Bunin's reasoning is quite convincing from the viewpoint of the formation of the spheroidal graphite. He brings the support of the sphere-forming action of the formation of cavities by self-diffusoin in one of his papers [18], making the observation that the shape of a section of a spheriodal graphite is always a polygonal one. (Should the cavities be formed by self-diffusion, the surface of the same would be made up by planes. This follows from the crystal structure.) In reality the section is generally a circular one, even when examined at great magnifications, and there are, if any, only a few corners in a section of a spheroidal graphite. This can be proved by photomicrographs, taken from the inner structure of a spheroidal graphite (see Fig. 17).

When summing up these explanations of the crystallization of spheroidal graphite, we come to the same conclusion as in the case of flake graphite. There is no univocal explanation of the laws, governing the crystallization and formation of spheroidal graphite, which should comprise all the observed facts without any contradiction.

2.3 The effect of the cooling rate

One of the first observations related with the metallography of cast irons was the fact that the cooling rate exerts a very great effect on crystallization.

Castings with very different properties can be made from the same material, only by varying the cooling rate. It was therefore only a natural stride to clear up quantitatively the effect of the cooling rate. This led to the different "diagrams" of cast irons, which take into consideration the effect of cooling rate.

The most commonly used diagram of this kind was that of F. GREINER and TH. KLINGEN-STEIN, determined in 1926. According to this, a material with a given chemical composition has a structure of ferrite + graphite — when produced by slow cooling — , later pearlite — graphite, then mottled and at last — when produced by rapid cooling — fully ledeburitic.

These diagrams have not been able to reproduce truly all the different kinds of structures, which are made possible alone by the variation of the cooling rate.

The inverse chill of the castings was for instance a well-known phenomenon, even at the time of World War I. This phenomenon could not be explained by any of these diagrams.

The supposition, that the effect of the cooling rate cannot be described in such an easy way, as in the case of these diagrams, was supported already in 1929, by an observation made by HEYKE and MAY [19]. They observed that at the point of the wedge-shaped samples, cast for the determination of the effect of the cooling rate there was in some cases some ferrite. This fact could hardly be explained by any conception based on the effect of the cooling rate and was called therefore "ferrite Type I" as against "ferrite Type II", which was formed on slow cooling of the sample. This distinction was not a lucky one, because it is out of question that they are both the same solid solution of iron and carbon. The difference lies only in the circumstances of their formation.

In the next two decades following this observation there were discovered many phenomena which are further interfering with the   once very simple — conception, related with the effect of the cooling rate.

Meanwhile it was established scientifically, that alloys produced with the same chemical composition but melted in different plants show different behaviour. The difference appears mainly in the inclination to become white. Different measurements were given in proof that iron, melted in reverberatory, electric or crucible furnaces shows a greater inclination to become white, than cupola-melted iron.

From this view even the quality of the burden is not indifferent — even in the case when the materials used are of the same composition. These "inherent" properties are too often over-

lapping the effect of the cooling rate and great caution is needed when using the diagrams of Greiner and Klingenstein.

Among other disturbing factors should be mentioned the effect of superheating and of modification and the very important differences in the shape of the graphite.

There are made every year some attempts to improve these diagrams. The most up-to-date ones [21, 22, 23] take into consideration many more factors than the diagram of GREINER and KLINGENSTEIN. They are nevertheless only of informatory character, such as is the diagram of Greiner and Klingenstein. For practical uses it is to be preferred to use the latter one, because it is handier and therefore more valuable.

3. The author's own experiments

3.1 The production of nodular cast iron without the application of any treatment

The possibility of the formation of spheroidal graphite in cast irons is a long-known fact. At first it was observed very seldom and only at the end of the last thirties succeeded ADEY [23] to produce intentionally nodular cast
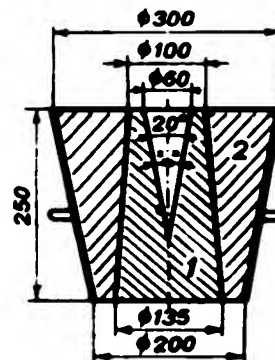
Fig. 1. Mould used for the casting of conical samples. 1 : Dried sand mould. 2 : Dry sand No. 6

iron. His method needed no treatment with either Mg or the like. (The action of these additions and their effect on the shape of the graphite was discovered only about a decade later.)

For this purpose we need to have — according to the patent application of Adey — an alloy of eutectic or hypereutectic composition, free from slag-inclusions and alloyed with silicon in an amount of at least 1%. He considered it as indispensable to have the metal strongly superheated and to contain no more than 0,008% sulphur. Even on fulfilment of all these conditions he succeeded to produce castings with spheroidal graphite only in that case, when the cooling was rapid.

The author carried out experiments in order to shed light on the problem, whether all the criteria — as laid down by Adey — must be taken into consideration.

104   I. KARSAY

The samples were melted in a furnace of the Tammann system, composed
of the following materials : soft iron powder (0,4% Mn, 0,071% S, 0,012% P.
0,16% Cu and no Ni, Cr or V), flake graphite (with ash-content 4,5%) and ferro-
silicon (94,8% Si). The crucible was made by turning on the lathe electrode
graphite. The temperature was measured by a Pt-PtRh thermocouple which

Fig. 2. The variation of the shape of the graphite with increasing cooling rate (the rate increases
from top to bottom). Unetched sample. Magn.   40.

contacted the bottom of the crucible and was controlled by an optical pyro-
meter.

The alloys with different chemical compositions were melted at a tempera-
ture of 1300 ± 20 °C and after a period of holding them at the same temperature,
were cast into dry conical sand moulds (Fig. 1). The composition of the moulding
sand was the following : 89% washed and dressed, filtered sand, with fineness
No. 6 (system DIN) ; 6% refractory lime : 4% water : 1% pectine.

The point of the conical samples — which cooled down at the highest rate — generally had a structure with spheroidal graphite (Fig. 2). The chemical composition of the cast samples varied between the following limits : 3,13 to 4,12% C, 0,41 to 4,26% Si, 0,30 to 0,32% Mn, 0,23 to 0,30% P, 0,06 to $0,07^o{}_o$ S.

Conclusions :

1. It is possible to produce an untreated and yet nodular cast iron even in the case when the material did not surpass in the molten state the temperature limit of 1300 °C.
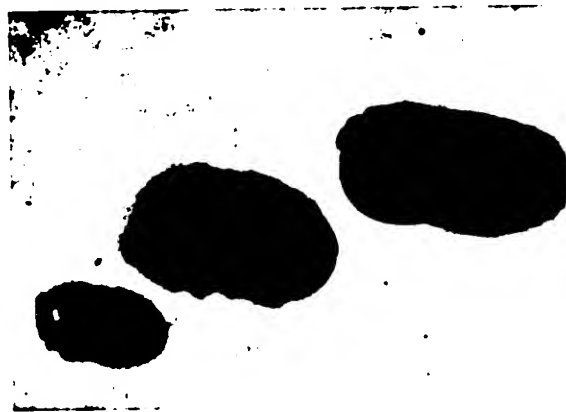
Fig. 3. Graphite in the form of spherical shells, crystallized into gas-cavities. Extracted from castings by solution in hydrochloric acid. Magn. ×20.

2. It is possible to produce an untreated and yet nodular cast iron even in the case when its sulphur-content is higher than $0,008^o{}_o$ — the limit, set by Adey.

3. It is not necessary to have a silicon-content in excess of 1%, in order to produce spheroidal graphite.

4. The cooling rate outweighs all else factors in view of the appearance of spheroidal graphite.

3.2 The production of cast iron with graphite of spherical shell form

When examining the fractures of the samples, the author found, after thorough preparation of the samples of the Mg-treated cast irons, some graphite in the form of spherical shells, especially at the edge of the samples (Fig. 3).

The author succeeded later to produce such graphite in the shape of spherical shells by two other methods :

a) Cast iron, heated slightly above its liquidus temperature was put suddenly under high vacuum ; on this occasion some particles were thrown out from the surface of the melt, at very high speed (at least 1 m/sec) (Fig. 4) .

When dissolving these particles in hydrochloric acid, the residue contained graphite in the form of spherical shells (Fig. 5).

Fig. 4. Globules thrown out of the melt on the action of vacuum. Magn. ×7.
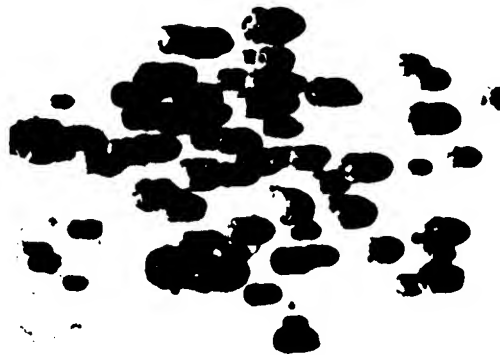
Fig. 5. Spherical shells of graphite inside the globules of iron shown in Fig. 4. (The shells are partly covered by a skeleton of silica, formed during dissolution in hydrochloric acid.) Magn. ×7.

The specific gravity of these small particles — with diameters less than 0,5—1,0 mm — was about 1,013 g/ccm. This is considerably less than the specific gravity of graphite and this gives another proof for the particles being hollow.

b) Molten hypereutectic cast iron was held under vacuum for a considerable time (about 10 hours) in a graphite crucible and then made to solidify in the same. The surface of the samples contains many graphite particles in the form of spherical shells (Fig. 6).

Conclusions :

1. *The graphite crystallized on the inside of gas-cavities ; in the first two cases this is definitely so and in the third case most probably.*
2. *The graphite may crystallize on the inside of gas-cavities.*

Fig. 6. Spherical shells of graphite at the surface of a cast bar of hypereutectic composition and molten in vacuum

Fig.7. Vertical section of a casting with inverse chill. Etched in 10% HNO₃ in alcohol. Original size

3.3 The production of castings with inverse chill

Some melts have been made in the Tammann furnace and cooled down in the same crucible, at a cooling rate of about 20 C/min. The crucible used in

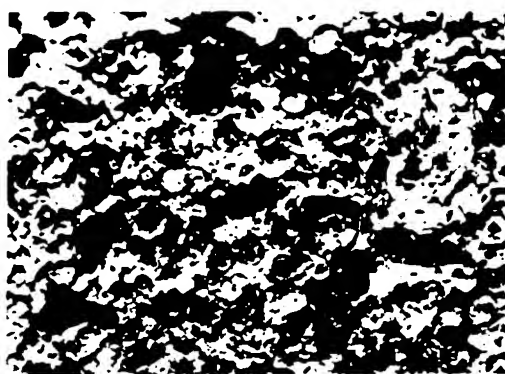108   I. KARSAY

this experiments was made of sillimanit, containing some 60% Al_4O_3; 38% SiO_2 1% Fe_2O_3 and 1% (CaO + FeO).

The castings showed in each case a more or less pronounced inverse chill. The section through such a sample is shown on Fig. 7.

Conclusion :

The described method results in each case in the production of castings with inverse chill. This allows for a more thorough examination of the question.

3.4 *The noise effect during solidification*

During melting experiments mentioned above a characteristic noise could be systematically heard at the beginning of solidification. The sound level of the same is very low ; it could be heard only in a quiet room.

Conclusion :

The noise cannot be produced directly by the solidification process, and it must therefore be supposed, that during the crystallization of cast iron there occur — at least in some cases — other physical processes too, which may lead to this sound effect.

3.5 *The effect of the cooling rate*

When summing up the literature related with the problem of the effect of the cooling rate, there were mentioned some important factors, omitted in the diagrams of Greine rand Klingenstein. As it is well known, these diagrams furnish some information relating to the solidification of cast iron, melted in cupola.

The author tried to show, whether the melting in a crucible was shifting the position of the lines of the same diagram. Conical samples were cast in the already described manner. The temperature of melting and of casting was 1300 ±20 °C. The material was held in molten condition for about 30 minutes. Besides of the conical samples, cylindrical samples were cast too, into permanent moulds.

The hardness was measured along the axis of the cones, employing a Vickers diamond pyramid indenter, a load of 10 kg. The time for applying the load was 30 seconds. Besides of the measurement of the hardness, the structure of the samples was determined too, in the plane of the axial section. In the case of the cylindrical samples, only the structure was determined in the section perpendicular to the axis of the sample.

The samples had the following chemical composition :

Test No.	% C	% Si	% Mn	% P	% S
Ll₀	4,12	0,41	0,32	0,028	0,070
Ll₁	4,08	1,38	0,32	0,03J	0,065
Ll₂	3,63	1,55	0,33	0,023	0,066
Ll₃	3,32	3,91	0,32	0,028	0,060
Ll₄	3,13	4,26	0,30	0,026	0,060

Chips were cut for the determination of the chemical composition by drilling radially at 3 points of the cone, at different heights.
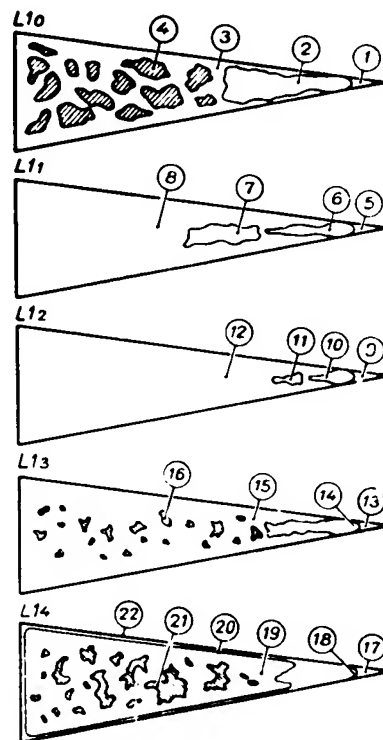
Fig. 8. The structure of the conical samples Ll_4 to Ll_0 in the plane of the axial section. Legend : 1 ledeburite + spheroidal graphite ; 2 ledeburite ; 3 pearlite + graphite ; 4 ledeburite + pearlite + graphite ; 5 ledeburite + spheroidal graphite ; 6 ledeburite + pearlite + graphite ; 7 pearlite + ferrite + graphite ; 8 pearlite + graphite ; 9 ledeburite ; 10 ledeburite + pearlite + graphite ; 11 pearlite + ferrite + graphite ; 12 pearlite + graphite ; 13 ledeburite + ferrite + spheroidal graphite ; 14 ferrite + graphite ; 15 pearlite + graphite ; 16 ferrite + graphite ; 17 ledeburite + ferrite + spheroidal graphite ; 18 ferrite + graphite ; 19 pearlite + graphite ; 20 ferrite + graphite ; 21 ferrite + graphite ; 22 pearlite layer on the surface of the conical sample

The results of the investigation of microstructure are shown on Fig. 8.

The microstructure of the cylindrical sample, cast from the material Ll_3 is shown on Fig. 9.

Conclusions :

1. The results of these experiments do not make possible to construct a diagram like the one made by Greiner and Klingenstein.

2. The appearance of ferrite is not a direct function of the cooling rate. This is especially true for the case of the conical sample cast from the material Ll_4. That part of the sample which cooled most rapidly, had a structure of ledeburite + ferrite + graphite, while going further along the axis of the sample toward that part, which cooled more slowly, there follows without any transition ferrite + graphite. Pearlite appeared only thereafter. The variation of the structure along the radius of the sample is even more interesting. The edge of the sample — in a thickness of about $50-100$ μ — is pearlitic. Immediately after this, we find a ferritic layer — of about 1 mm thickness — which is super-
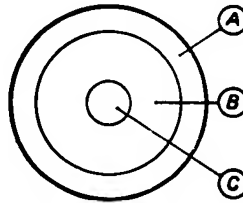
Fig. 9. The structure of the cylindrical sample Ll_3 in the plane perpendicular to its axis. *Legend :* A ledeburite + spheroidal graphite ;   B pearlite + ferrite + graphite ;   C ledeburite + pearlite + graphite

seded by pearlite + graphite. Finally in the neighbourhood of the axis, which portion cooled most slowly, there appears again the ferritic structure (Fig. 8).

3. The apparition of cementite is not a direct function of the cooling rate. This is especially true in the case of the structure of the cylindrical sample, cast from material Ll_3. The outer part of the rod, which cooled most rapidly, was ledeburitic, but the zone around the axis, which cooled most slowly, had a white structure too (Fig. 8).

4. The diagram made by GREINER and KLINGENSTEIN can be regarded only as a simple tool, giving general information, which is valid only under certain conditions. It does not refer to every part of the casting, for instance to the outest case, but only to the structure of the bulk of the casting. It does not represent either truly the variation of the structure of cast iron, cooled very rapidly.

5. It follows from all that has been said, that the cooling rate has only an indirect effect on the crystallization of cast iron.

3.6 More detailed study of the shape and structure of the graphite flakes

This question is discussed only very briefly in the related literature. The shape of the flakes was studied by several investigations of F. ROLL [24], P. SCHAFMEISTER [25] and J. T. MACKENZIE [26], but these investigations refer only to "eutectic flakes" and the applied experimental methods do not provide for a high accuracy of the results.

As to the question of the flakes, it is well known, that each flake consists of many crystallites and that the basal planes of the same are parallel to the basal face of the flake.
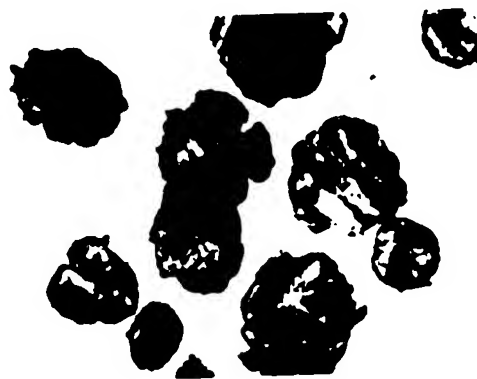
Fig. 10. Hypereutectic flake graphite. Extracted from the castings by solution in hydrochloric acid. Magn. ·30.

For the purposes of these investigations the graphite flakes were generally extracted from the matrix and put under the binocular microscope. Extraction was made with hydrochloric acid. The silica skeleton, which forms on this occasion, can be separated very easily from the graphite and was therefore removed by mechanical means.

The shape of the "hypereutectic graphite flakes" can be seen on Fig. 10. The flakes are in this case like circular plates.

The extracted hypereutectic graphite flakes can be split very easily into two parallel plates. At first sight, this phenomenon could be explained by the easy slip of the graphite in the direction parallel to its basal plane. Later it was proved, that the easy splitting must have another cause, because further splitting could not be accomplished without the total demolishing of the flake.

When examining the possibilities for splitting the hypereutectic flakes, the structure of the sections of the same was studied too. It could be shown, that in a properly prepared section of a flake there is always a partition (Fig. 11). This partition line can be shown even in the case of eutectic flakes.

Conclusions :

1. The shape of the extracted hypereutectic graphite flakes is generally a circular plate or the like.

2. The extracted hypereutectic graphite flakes consist generally of two parallel plates which can be separated very easily. The line parting these two plates is discernible already at a magnification of about 500, provided the metallographic specimen is prepared with great care.

Fig. 11. The partition line in the center of a hypereutectic flake graphite. Unetched sample. Magn. ×300.

3. *Based on the material already discussed it may be mentioned again, that besides of the 3 already known shapes of the graphite (flake, quasi-flake or compacted and sphere) there exists also a fourth one, that of a spherical shell.*

3.7 The study of the structure of the surface of graphite of spherical shell form

As the first step only graphite extracted from cast iron, treated with Mg was studied.

The extraction was made by the same method as described in 3.6. The investigation was made with the help of a binocular microscope, while the photomacrograph was made with the help of a collapsible photographic apparatus.

The photo-macrograph is to be seen on Fig. 12. The surface is full of wrinkles.

Conclusion :

On the surface of graphite extracted from cast iron, treated with Mg, runs a characteristic circular or spiral pattern.

3.8 Experiments to show the effect of degassing

The greatest part of the experiments herein described (more than 30 melts) was conducted in order to clear up the effect of the removal of gases.

Melting was done in a Tammann furnace, in sillimanite crucibles. The removal of the gases was tried by suction. This was done with the help of a rotary pump of 1,5 HP, made by Balzers'. The pressure was measured with a mercury manometer, having a scale with divisions of one mm. By this way a variation in the pressure of about 0,5 mm could be detected, or estimated.

Fig. 12. The pattern on the surface of a graphite in the form of spherical shell, taken from a casting, treated with Mg. Magn. ⋅ 12.

The removal of oxygen could not be accomplished in the desired measure with the help of the given apparatus. The attained vacuum was never greater than 10^{-3} atm.

The samples melted under vacuum had a graphite, corresponding to AFA-ASTM Type D.

Based upon the material discussed up to now, it is already out of question, that degassing exerts some effect on the crystallization. It seems therefore reasonable to continue the experiments for the removal of gases, supposed that a more perfect method could be found for this purpose.

The accomplishment of the task set was not possible.

3.9 Experiments to study the effect of some gases

Several experiments were tried to clear up the effect of some gases. The gases introduced into the furnace were purified, conducting the same through copper-turnings, held at a temperature of 600 C, silica-gel, potassium-hydroxide, phosphoric anhydride and yellow phosphorus. Bubbling through the melt was

accomplished with the help of a sillimanite tube, the end of which reached to the bottom of the melt.

Neither of these experiments can be regarded as reliable, chiefly because the introduction of the said gases was not preceded by a sufficient removal of the other gases (see Section 3.8). The contradictions with respect to this question which are to be met in the literature can be traced back to this point.

There is however a single experiment which should be mentioned. The fracture of a metal, through which hydrogen was bubbled for over 10 minutes and the chemical composition of which was : 4,26% C, 0,21% Si, 0,39% Mn,

Fig. 13. Fracture of cast iron, treated with hydrogen. ×0.5.

0,041% P and 0,064% S (analysed after the treatment), can be seen in Fig. 13. It is very interesting that the surface of the sample, which had the most intimate contact with hydrogen, is grey, whereas the core, which was in the least contact with hydrogen, is white. It is of course impossible to draw far-reaching conclusions from a single experiment. But it is also out of question that the gases exert some effect on the crystallization and it would be therefore very reasonable to continue the investigation of the said problem.

The solution of the task set was not attained.

4. A hypothesis for the explanation of the crystallization of graphite in cast irons

4.1 The existence of some "internal surfaces"

When reviewing the literature, attention was drawn on the contradiction between the structure of the graphite flakes and the supposed mechanism of their formation. The enrichment of the crystallites of the graphite, as in the

case of either the flake graphite or the spheroidal graphite, makes necessary the existence of some surfaces, which arrange and collect the newly formed graphite monocrystals. The parallelism of the crystallites of the flake graphite could be explained by some field of magnetic forces as well, but this supposition is in our case out of question. If we suppose, however, that the arrangement — and perhaps the formation as well — of the crystallites takes place on some definite surfaces, the explanation is quite obvious.

There are numerous observations, which support the view that such surfaces really exist in the solidifying melt and the crystallization of the graphite goes on inwards into some gas-cavities — and this is done independently, whether the result is flake graphite or spheroidal graphite.

We shall note some of these observations.

a) On the surface of hypereutectic pig iron, especially on the surface of its shrinkage cavities, one may find some graphite-kish. This is in the reality, however, nothing else, than a heap of graphite flakes of different orientations. It can be hardly imagined, that during crystallization these graphite flakes emerged from the iron melt. It is also very improbable, that the graphite flakes formed inside the melt could have passed through the surface of the melt, partly because of the high surface tension of the molten iron and partly because of the relatively low strength of the graphite. (σgraphite 2 kg mm².) One would expect at the most to have the graphite flakes heap up and cover the surface of the melt.

This phenomenon could be explained by supposing the formation of a foam on the surface of the liquid iron, made up by gas-bubbles and a thin liquid film of iron, parting them. The graphite could have been crystallizing on the walls of the gas-cavities of the foam, but after the fissure of the foam — because of variation in the existing pressure — it forms an entirely irregular heap. The author succeeded to trace in the graphite-kish some iron globules which were formed as a result of the fissure, very often on some definite places of the surface of the flakes.

b) According to the opinion of PLASKOWSKI [27], the eutectic spheroidal graphite crystallizes inside the primary dendrites of austenite, whereas the flake graphite is arranged interdendritically. WITTMOSER [11] advocates a similar opinion. The photomicrographs, which Wittmoser shows in support of his views, do not, however, prove the second part of his supposition. It is out of question that the spheroidal graphite was enveloped by a crust of primary austenite, but the photomicrographs are proving — according to the author — the very likely supposition that the flake graphite was also formed inside the primary austenite. This later view is also supported by practical experiences of many years. It is well known, that the graphite is — with the exception of a few cases — more or less uniformly distributed, even in the cases of hypoeutectic composition of the cast iron. It is therefore not accidental that practical experts are considering as the "eutectic graphite distribution" not this, but that exceptional case, where the primary dendrites of austenite are easily perceptible and the graphite is arranged only interdendritically.

The experiment proving that from melts having the same composition i. e. having the same saturation we may produce a material with random or even a material with "eutectic graphite distribution", gives at the same time the correct proof of the view, that the graphite of random distribution cannot be regarded as a "normal" eutectic graphite. PIWOWARSKY [28] made experiments by casting the same material into permanent moulds and into sand moulds. The chemical composition was the following : C 3.2%; Si 2.2%; the saturation factor was 0.85. Fig. 14 shows the sample, cast into sand, while Fig. 15 shows that, which was cast into the permanent mould. Both samples were heated to a temperature above 800 C then slowly cooled down with the furnace to 650 C. The result was a ferritic structure. Both materials were highly graphitized before the anneal. As it can therefore be seen, material of the same composition produces on rapid cooling an "eutectic graphite", and on slow cooling graphite of random distribution. It is quite obvious that in the latter case the graphite took place inside — at least partly in primary austenite.

All the graphite — or at least a portion of it — is thus built up by the diffusion of carbon through the solid solution. The controlling factor of the

growth of the crystal is, however, in such circumstances — as already shown
by Bunin [15] — the rate of formation of vacant places. The crystallization
of graphite can take place only at those places which were cleared by the iron
atoms. The formation of vacant sites requires however the self-diffusion of
iron atoms, which is a very slow process. It can be hardly imagined, that in the
few seconds disposable during solidification, cavities of the required dimensions
could be formed [29].

But there is more probably no need for the formation of vacant sites by
such a self-diffusion. The cavities are already present at the outset of the crystal-
lization of graphite, in the form of gas-bubbles, on the inside of the austenite

Fig. 14. Ferritic cast iron. Taken from Ref. [28]

dendrites, or better to say — as we shall see it later — on the inside of special
austenitic formations, crusts. This is the reason of their random distribution.

The crystallization of the graphite thus begins on the walls of these gas-
bubbles. Under favourable conditions the cavities get entirely or almost entirely
filled up by graphite. There is time, however, usually only for the formation
of a thin spherical shell, which is ruined during the further crystallization and
changes its shape. In the first case there is formation of spheroidal graphite
and in the second case that of flake graphite.

There is therefore only a single fundamental condition for the formation
of graphite : the presence of gas-bubbles or cavities during crystallization.

4.2 The presence of gas bubbles in liquid iron and their dimensions

Are there really in the melt such supposed gas-bubbles?

Gray cast iron usually contains about $7-12$ % by volume of graphite.
According to the afore-said, it is necessary to have during crystallization in

the case of spheroidal graphite exactly the same quantity of gas, in the case
of flake graphite, however, considerably more, about 20 · 10⁻⁴, by volume.

The determination of the gas-content is hardly reliable. It may be
nevertheless accepted, that grey cast iron always contains some 0.3 – 0.5
standard ccm oxygen per gram, not to speak of the other gases. This quantity
is a multiple of the quantity needed.

The further studies are confined to the system Fe – C – O. It has to be
remarked that the other constitutional elements, which are always present
cause only a quantitative change and do not change the character of the
process.

Oxygen is present in molten iron in the form of FeO. (The solubility
of gaseous oxygen and carbon monoxide can more probably be neglected.)
The solubility of FeO diminishes, however, strongly with reduction of the
temperature. Solid cast iron contains practically no dissolved FeO. During
cooling down there results therefore sooner or later a supersaturation of the
melt with respect to FeO, and the latter begins to coagulate. This means that
at some preferred places of the melt the reaction

$$FeO + C = Fe + CO$$

looses the equilibrium — if there was any — and carbon monoxide begins
to form.

The newly formed gaseous CO surrounds the FeO-particle. The latter
cannot escape from the gas-bubble because for the crossing of the surface of
the same it would be necessary to have accumulated very much energy. Thus
the FeO and the gas-bubbles are slowly rising together in the melt. If all the
bubbles could reach the surface of the melt and all FeO would be carried to
the slag, this would mean the complete removal of gases. The already men-
tioned oxygen determinations prove, however, that the short period which
elapses until the complete solidification of the melt, is far from being enough
for the removal of all gas-bubbles.

It is very interesting to study from this view the question of the forma-
tion of the so-called "inverse chill". If complete removal of the gas-bubbles
could be reached, the castings would crystallize entirely white, even on slow
cooling, just because there are no gas-cavities. This can, however, hardly
be realized under practical conditions. In the inner part of the casting there
is removal of the gases by flotation, but the oxides adhering to the walls of
the crucible or floating to the surface of the melt are producing uninterrupt-
edly new bubbles. The metal is solidifying in this case on the outside of the casting
with grey and on the inside of the same with white fracture. The author suc-
ceeded to produce in the course of his experiments castings with inverse chill
at a cooling rate of about 20° C/min (see Fig. 7).

If all that has been told, is correct then there exists the possibility of **computing the approximative size of the bubbles.** With given space of time **between the beginning and the end** of the solidification, given height of the **liquid column, viscosity of the molten** cast iron and specific weight of the **same, the radius of the bubble can** be computed with the help of the Stokes-equation.

For the given set of conditions, the radius of the bubble, ϱ amounts to 37μ and the mean length of the flakes, l amounts to 74μ. (We made the supposition that the spherical shell flattens into a thin circular plate. Though this assumption is not quite correct, in the given case it may be accepted.) The real length of the flake graphite in the grey part of our experimental cast iron amounts to 110μ. The accord is sufficient.

4.3 The process of crystallization

When moderately cooled, cast iron always contains some gas-bubbles. Too fast cooling may result in the FeO remaining in solution : in this case there is no development of gases and the solidification results in a graphite-free casting.

Supposed we have an alloy of hypereutectic concentration, the solidification begins with the formation of primary austenite crystals. These crystallize on the surface of the gas-bubbles. Reduction of the FeO is an endothermic reaction, and the coolest points of the liquid are therefore on the surface of the bubbles.

The bubbles get an envelope of a solid shell of austenite. In the mass of this shell there is a considerable diffusion of the carbon towards the inside of the sphere, from the moment of the formation of the shell onward. This question shall be discussed a little later. The carbon atoms may reach the inside of the shell and the continuation of the reduction of the FeO is thereby secured.

Some experiments carried out make it probable that the reduction of the FeO results in a very high pressure, and the spherical shell bursts.

In Figs 4 and 5 were shown some particles which were thrown out of the melt on the action of vacuum. The velocity of the said particles was in the moment of their exit at least 1 m sec. The energy these particles needed for crossing the surface of the melt and getting accelerated in a highly viscous liquid, could not be acquired by any other means than the bursting of one or more nearby austenite shells.

The observation of noise during the solidification of cast iron — mentioned in Section 3.4 — also supports the existence of the bursting mechanism.

The burst austenite shells and graphite particles are frozen in the melt.

What is happening to the new gas-bubbles formed in consequence of bursting? Their pressure is not further increased — for lack of FeO — but on the contrary is reduced with reduction of the temperature, and they get sooner or later flattened, after having received a graphite shell, which crystallized on their surface.

Fig. 15. Ferritic cast iron. Taken from Ref. [28]
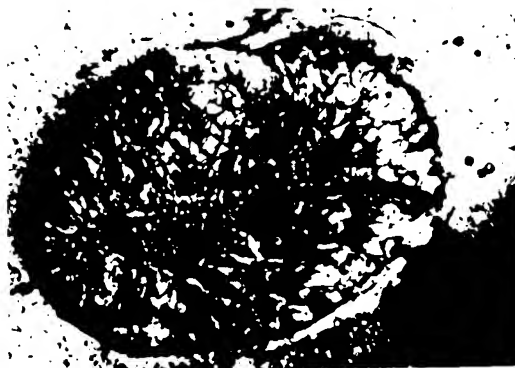
Fig. 16. The partition line in the direction of the major axis of the section of an ellipsoidal graphite. Etched by the cathodic vacuum etching method. (Photomicrograph taken with electron microscope.) Taken from Ref. [36]

What is happening to the gas inside the bubbles? It remains more probably in the center of the graphite flake and forms there a thin disclike cavity. This can be related with the easy splitting of the graphite flakes, already discussed in Section 3.6. Width of the lines which can be seen in the section of a graphite flake is corresponding to the calculated height of the flattened gas-cavity (see Fig. 11).

There is a partion line to be seen in the direction of the major axis of the section of an ellipsoidal graphite, shown by H. TSUCHIKURA, T. KUSAKAWA and T. OKUMOTO [36] (Fig. 16).

4.4 The mode of formation of spheroidal graphite

After all that has been said, the necessary conditions for the formation of spheroidal graphite can be formulated very easily. It is only necessary, that the gas-bubbles formed during the solidification get entirely filled up by graphite.

This seemingly simple condition involves however many problems.

The first problem immediately arises as we revert the condition: if more gas-bubbles are formed than what can be filled up entirely with the disposable graphite — which is 7—12 % by volume — we get some flake graphite and if there are less bubbles, some cementite will be found too.

The second related problem: it is not indifferent of what size these bubbles are. If the necessary amount of gases is distributed in the form of large bubbles, the graphite will not fill up these cavities — for lack of time —, and besides of the flattened out spherical shells there will be some isolated cementite too. The original stipulation must therefore be modified in the following manner: the melt should contain gas in an amount of 7—12 % by volume, and the gas-bubbles should be small, their radii should not surpass 10—100 μ. (The latter condition is seemingly not too rigorous, but in real cases the allowable size of the bubbles is further limited by the cooling rate as well. In the case of slower cooling greater bubbles may be filled up as well.)

It is generally accepted, and in this paper it has been discussed too, that a cast iron which is suitably degassed and cooled down at a corresponding rate, may crystallize with spheroidal graphite [23, 30, 31]. The conditions to be met, in order to attain this purpose are, however, so rigorous, that they cannot be fulfilled under practical conditions of industrial production.

The possibilities of industrial production of nodular cast iron were first secured by the discovery of MORROGH and WILLIAMS [32], who found that treatment with cerium results in cast iron with spheroidal graphite. Further research detected many elements which exert a similar effect on the crystallization of graphite.

The common property of all the suitable nodularizing materials is a thorough degassing action. A suitable amount of these nodularizing additions may result in a corresponding level of the gas-content.

A further action of the nodularizing additions is that on the surface tension of the melt. Both actions effect a corresponding variation in the size of the gas-bubbles. A reduction of the gas-content causes undoubtedly the

reduction of the size of the gas-bubble. The increase of the surface tension causes a similar effect. In accordance with these conditions MARINCEK and his coworker [11] found — as already discussed — upon a treatment with Mg an increase of about 50 % of the surface tension of the melt.

The mode of formation of spheroidal graphite is more probably a more complex problem than that already outlined. It is readily conceivable, for instance, that in this case we have to face not carbon monoxide, but some other gas. It is a very interesting observation that a fresh fracture of nodular cast iron develops upon the action of the moisture content of the air some gas. It is therefore possible that — following this track — we may find out in time much more about the mode of formation of the spheroidal graphite. In the meanwhile, there is no reason for further reasoning because there are too few actual observations, objective data.

Just the same must be said about the question of the graphitization of white cast iron. It may be supposed that the FeO which was retained in solution, in consequence of fast cooling, gets coagulated when heated and develops gases. The graphite crystallizes into these generally irregular, clustered cavities. It is worth while to mention in this connection that the reduction of FeO with carbon can be accomplished only a temperatures above 725 C. Annealing at temperatures lower than this, has therefore no graphitizing action. This is in accordance with practical findings, because the lowest possible temperature of tempering, corresponding to a cycle of t — is about 700 C. The supposition that in the case of spheroidal graphite not — or not only — the FeO-content is associated with the development of gases, is made probable among others by the fact that the graphitization of a white fractured — although Mg-treated — cast iron can be accomplished at a temperature much lower than the above mentioned, i. e. at 500 550 C [37].

It is therefore premature and not sufficiently accounted for to discuss in detail the effect of the different alloying elements. It is, however, very probable that they alter mainly the gas-content and surface tensions of the melt, as well as the conditions for diffusion, and hereby exert their action on the crystallization of graphite.

4.5 The mechanism of crystallization of graphite into the cavities

A further question to be discussed is a problem which can be followed very difficultly by experiments, i. e. how the graphite crystallizes into the gas-cavities?

After the formation of a graphite crust of limited thickness, further growth must proceed through the same. It is, however, hardly conceivable that the carbon penetrates this graphite layer of ever increasing thickness by selfdiffusion. The time available is supposedly too short.

122   L. KARSAY

The possibility of such a mechanism is, however, more than a mere supposition. The author produced several microphotographs of graphite in the form of spherical shells, having a microscopical wall-thickness.

The next few – already discussed – observations make it also probable, that the graphite grows from the outside inwards.

The hypereutectic graphite flakes have generally the form of circular plates or the like (see Fig. 10). This cannot be accounted for by a "rounding off" effect of the surface tension. This action would prevent first of all the formation of the flakes of large specific surface.

Fig. 17. Spheroidal graphite. Etched by the cathodic vacuum etching method. (Photomicrograph taken with electron microscope.) Taken from Ref. [56]

The flattening out of an originally spherical shell into a circular plate is a much more acceptable explanation. The partition line of the two halves can be made visible, as already discussed. The relatively easy splitting of the hypereutectic flakes into two parallel plates was mentioned too.

H. TSUCHIKURA and his coworkers made photomicrographs of some regularly shaped spheroidal graphite particles as well (Fig. 17). The sectional plane passes in this case more or less exactly through the center of the sphere. It can be seen that the contour lines parallel to the basal plane are at the border of the section more regular, and in the middle of the section almost entirely irregular. This proves again a growth from outside inwards.

How this crystallization into the cavity is yet made possible?

On the surface of a graphite in the form of a spherical shell, extracted from a melt treated with Mg, there is a pattern which is similar to that found by H. BUCKLE [33] when depositing Zinc on a cooled plate. It is nevertheless hardly conceivable that graphite forms from the gaseous phase. In the volume occupied by carbon monoxide there is carbon in a concentration which is several thousand times less than necessary.

The possibility of growing by self-diffusion cannot be excluded too. This case will be discussed somewhat later. There is another possibility of the carbon atoms entering at some preferred points the surface of the cavity and growing laterally on to the already existing groupings. It may be supposed too that the carbon atoms, shifting the already crystallized layers toward the centre of the cavity, are forming new layers and the process repeats itself.

This question has to be decided by further experiments.

The last question to be discussed is that whether there is any principal contradiction in supposing the diffusion of the carbon toward the cavities.

This diffusion cannot be controlled by concentration or temperature gradients. The only conceivable driving force of the diffusion is a stress-gradient. We may choose for a model in our case a thick-walled spherical shell uniformly compressed on the outside and the inside. The tangential stresses set up in the outer part of the shell are compressive stresses and those in the inner part are tensile stresses [34].

The effect of stress-gradients on diffusion was fundamentally investigated by KONOBEJEVSKY [35] at least qualitatively. According to his findings diffusion is always directed from the compressed volume toward the extended one. This is exactly the condition for the discussed problem because by reducing the free gas-volume the internal gas-pressure becomes greater and greater and as a result, the tensile stress in the inner wall grows too. That is the necessary condition for the possibility of the self-diffusion of graphite.

This also gives an answer to the question as to why there are encountered very few large cavities in the centre of the spheroidal graphites, although according to the afore-said there always must remain some small cavity. This is the space for the highly compressed gases.

The understanding of the process in question would be nearer, if there were an answer to the problem as to the role of the substance of the gases. The experiments carried out up to now give no reassuring answer to this problem. It is nevertheless worth mentioning remembering the experiments discussed in Section 3.9 that hydrogen which is usually qualified as exerting a strong effect toward a white fracture, seems to support graphitization. The reason for this seeming contradiction is more probably the neglect of the removal of other gases especially of the oxygen while examining the effect of hydrogen. As long as there is oxygen in the melt the treatment with hydrogen undoubtedly diminishes the gas-content of the melt and hereby exerts a whitening effect.

As already mentioned, the experiments carried out up to now do not allow for a definite decision of the problem, though it seems that the substance of the gases makes no difference as to the mode of graphitization

124   L. KALSAY

REFERENCES

1. *Уманский, Я. С., Финкельштейн, Б. Н., Блантар, М. Е.*: Физические основы металловедения, Москва, 1949. (in Russian).
2. PIWOWARSKY, E., WITTMOSER, A.: Giesserei Techn. Wiss. Beihefte, 1 (1949), pp. 3.
3. DE SY, A.: Metal Progress, 57 (1950), pp. 774.
4. GILLEMOT, L.: Proceedings of the Technical Section of the Hungarian Academy of Sciences, III, pp. 47 (in Hungarian).
5. KALSAY, L.: The Foundry, 2 (1953), pp. 25 (in Hungarian).
6. *Гиршович, Н. Г.*: Литейное производство, 1 (1951), 17 (in Russian)
7. *Гиршович, Н. Г.*: Литейное производство, Москва
9. DE SY, A.: Metal Progress, 59 (1951), pp. 798.
10. THALL, P. M., CHALMERS, B.: J. Inst. Metals, 77 (1950), pp. 79.
11. GRUTTER, K., MARINČEK, B.: Schweizer Archiv, June 1953, p. 171.
12. BUTTNER, H. E., TAYLOR, E. H., WULFF, J.: American Foundryman, 20 (1951), pp. 49
13. WITTMOSER, A.: Giesserei, 40 (1953), No. 1, p. 9.
14. WITTMOSER, A.: Giesserei, 40 (1953), No. 1, p. 10.
15. *Бунин, К. П., Иванцов, Г. П.*: Доклады Акад. Наук СССР 72 (1950), N 6.
16. *Лахтман, В. П., Смирнова, Н. П.*: Доклады Акад. Наук СССР 86 (1952) ст 1151.
17. *Бунин, К. П., Спак, Г. М.*: Литейное производство 1954, N 5, ст 29.
18. *Бунин, К. П., Черновол, А. В.*: Доклады Акад. Наук СССР 95 (1954)
19. HEIKE, W., MAY, G.: Paper in Giesserei, 16 (1929), pp. 625, taken from Piwowarski: "Gusseisen", 1951.
20. LAPLANCHE, H.: Metal Progress, 52 (1947), pp. 994.
21. SIPP, K.: Arch. Eisenhuttenwesen, 11 (1910/10-11) pp. 267.
22. *Гиршович, Н. Г.*: Чугунное литье Москва, 1949 ст 107 (in Russian)
23. ADEY, C.: Giesserei, 33-35 (1948), pp. 63.
24. ROLL, F.: Paper in Giesserei, 15 (1928), pp. 1250, taken from Piwowarski: "Gusseisen", 1951.
25. SCHAEMEISTER, F.: Arch. Eisenhuttenwesen, 10 (1936), 373, pp. 221.
26. MACKENZIE, J. T.: Paper in A. F. M. A., Techn. Publ. No. 1711 (1944), taken from Piwowarski F., "Gusseisen", 1951.
27. PIASKOWSKY, I.: Prace Inst. Odlew., 2 (1952), pp. 93 (in Polish).
28. PIWOWARSKY, F.: "Gusseisen", 1951, pp. 132 (Figs. 18, 20)
29. BIRCHENALL, C. E., MEHL, R. F.: Trans. AIME, 188 (1950), pp. 144.
30. ZORKOCZY, B.: Proceedings of the Technical Section of the Hungarian Academy of Sciences, III, pp. 179 (Hungarian).
31. KIRPELAY, K.: Die metallurgischen und metallographischen Grundlagen des Gusseisens, Berlin, 1928.
32. MORROGH, H., WILLIAMS, W. J.: J. Iron a. Steel Inst. (1948), pp. 306.
33. HANLA, F.: Kristallchemie u. Kristallphysik metallischer Werkstoffe, Leipzig, 1951, pp. 55.
34. *Бочвар, Н. Н.*: Теория литейных процессов, Москва, 1953, ст 194.
35. KONOBEJEVSKY, S. J., SELISSKY, J. P.: Phys. Z. d. S. R. I (1934) pp 459, taken from Umanski etc. Ref. (1).
36. Original photomicrographs from "The observation of graphite in cast iron by means of cathodic vacuum etching", lecture read at the London Conference of Electron Microscopy, 1954, By kind permission of the Authors (H. Tsuchikura, F. Kusakawa and T. Okamoto).
37. Personal communication of Mr. B. Kocze. Cand. Sci. of the Hung. Acad. of Sci.

SUMMARY

The author described his experiments conducted for further clearing up of the problems related with the structure of the graphite and the phenomena occurring during the solidification of cast irons. He succeeded — among other things — to demonstrate besides of the three known 3 shapes of graphite a fourth one (spherical shell).

The investigations and observations made during the experiments cannot be utilized directly for the solution of problems related with the industrial production because the research was made entirely on theoretical lines. The results have only an influence on the problems of the industry, in so far as they are helpful towards a sound better understanding of the mode of crystallization of graphite.

The hypothesis, laid down in this paper, may support further scientific research. Based on this it would be expedient to organize systematical experiments for the solution of particular problems of the industry. It would be necessary, however, at the same time to prove or to disprove the assumptions related with the said hypothesis.

О КРИСТАЛЛИЗАЦИИ ГРАФИТА В ЧУГУНЕ

Канд. техн. наук Л. КАРШАИ

РЕЗЮМЕ

Сообщаются опыты, которыми исследовалась не только наличность и сочленения явлений, происходящих в структуре графита и в чугуне во время затвердевания. В результате проведенных опытов, между прочим, удалось наряду с известными до сих пор тремя видами графита показать существование еще и четвертого вида (шаровой оболочки).

Естественно, что проведенные исследования и опытные наблюдения, так как они часто теоретического характера проведенных исследователеской работы, не могут быть использованы непосредственно для решения промышленных проблем. Достигнутые результаты интересны для промышленности только постольку, поскольку они позволяют более основательно ознакомиться с процессом кристаллизации чугуна.

Для дальнейшей исследовательской работы считается важной применяемая гипотеза. На основе этой гипотезы, принимаемой в качестве программы работы с одной стороны, было бы целесообразным организовать опыты в интересах решения отдельных промышленных проблем, однако в то же время предположения гипотезы независимо от их правильности или ошибочности требуют опытного доказательства.

SUR LA CRISTALLISATION DU GRAPHITE DANS LA FONTE

L. KARSAY

candidat des sciences techniques

RÉSUMÉ

Les expériences relatées dans cette étude ont été effectuées en vue de mieux connaître la structure du graphite et les phénomènes qui se produisent au cours de la solidification de la fonte. Ces expériences ont prouvé, entre autres, l'existence d'une quatrième forme du graphite (écorce sphérique), en plus des trois formes connues jusqu'à présent.

Les examens et les observations aux cours des expériences ne sont naturellement pas directement utilisables à la solution des problèmes industriels, les recherches ayant un caractère purement théorique. La valeur industrielle des résultats consiste dans leur contribution à une connaissance plus approfondie de la cristallisation de la fonte.

L'auteur estime que l'hypothèse communiquée dans cette étude sera importante pour les recherches ultérieures. Elle pourra servir utilement le programme de travail pour l'organisation des expériences en vue de la solution de certains problèmes industriels; toutefois, les différents points de l'hypothèse demandent encore d'être vérifiés par des expériences.

ÜBER DIE KRISTALLISATION DES GRAPHITS IM GUSSEISEN

L. KARSAY

Kandidat der technischen Wissenschaften

ZUSAMMENFASSUNG

Die in der vorliegenden Arbeit geschilderten Versuche wurden vom Verfasser zur weiteren Klärung der Graphitstruktur und der Vorgänge während der Erstarrung des Gusseisens durchgeführt. Als Ergebnis der Versuche ist es unter anderem gelungen, neben den bisher bekannten drei Graphitformen auch eine vierte (Kugelschale) nachzuweisen.

Natürlich können die Untersuchungen und experimentellen Beobachtungen, die der Forschungsarbeit einen ausgesprochenen theoretischen Charakter hatte, nicht unmittelbar zur Lösung von industriellen Problemen benutzt werden. Die Ergebnisse sind aber insofern für die Industrie von Bedeutung, als sie die Kenntnisse über die Kristallisation des Gusseisens erweitern. Für die weitere Forschungsarbeit hält der Verfasser die in der Arbeit mitgeteilte Hypothese für wichtig. Mit dieser als Arbeitsprogramm wäre es einerseits zweckmässig, Versuche im Hinblick auf die Lösung von einzelnen industriellen Problemen zu organisieren; andererseits warten aber auch die hypothetischen Annahmen selber auf eine experimentelle Bestätigung.

Les Acta Technica paraissent en russe, français, anglais et allemand et publient des travaux du domaine des sciences techniques.

Les Acta Technica sont publiés sous forme de fascicules qui seront réunis en un volume.

On est prié d'envoyer les manuscrits destinés à la rédaction et écrits à la machine à l'adresse suivante :

Acta Technica, Budapest 62, Postafiók 440.

Toute correspondance doit être envoyée à cette même adresse.

Le prix de l'abonnement est de 110 forints par volume.

On peut s'abonner à l'Entreprise pour le Commerce Extérieur de Livres et Journaux «Kultura» (Budapest, VI., Sztálin út 21. Compte-courant No. 43-790-057-181) ou à l'étranger chez tous les représentants ou dépositaires.

The Acta Technica publish papers on technical subjects in Russian, French, English and German.

The Acta Technica appear in parts of varying size, making up one volume.

Manuscripts should be typed and addressed to :

Acta Technica, Budapest 62, Postafiók 140.

Correspondence with the editors and publishers should be sent to the same address.

The rate of subscription to the Acta Technica is 110 forints a volume. Orders may be placed with „Kultura" Foreign Trade Company for Books and Newspapers (Budapest, VI., Sztálin út 21. Account No. 43-790-057-181) or with representatives abroad.

Die Acta Technica veröffentlichen Abhandlungen aus dem Bereiche der technischen Wissenschaften in russischer, französischer, englischer und deutscher Sprache.

Die Acta Technica erscheinen in Heften wechselnden Umfanges. Mehrere Hefte bilden einen Band.

Die zur Veröffentlichung bestimmten Manuskripte sind, mit Maschine geschrieben, an folgende Adresse zu senden :

Acta Technica, Budapest 62, Postafiók 140.

An die gleiche Anschrift ist auch jede für die Schriftleitung und den Verlag bestimmte Korrespondenz zu richten.

Abonnementspreis pro Band 110 Forint. Bestellbar bei dem Buch- und Zeitungs-Aussenhandels-Unternehmen »Kultura« (Budapest, VI., Sztálin út 21. Bankkonto Nr.: 43-790-057-181) oder bei seinen Auslandsvertretungen und Kommissionären.

A kiadásért felel az Akadémiai Kiadó igazgatója

40072,56 — Akadémiai Nyomda — Felelős vezető: Puskás Ferenc